ScienceDirect

Physica B: Condensed Matter
Volume 547, 15 October 2018, Pages 64-71

Rietveld, cation distribution and elastic investigations of nanocrystalline $Li_{0.5+0.5x}Zr_xFe_{2.5-1.5x}O_4$ synthesized via sol-gel route

Jitendra S. Kounsalye, Ashok V. Humbe, Apparao R. Chavan, K.M. Jadhav

Show more

Share Cite

https://doi.org/10.1016/j.physb.2018.08.007
Get rights and content

Highlights

- The monovalent and tetravalent substitution in spinel ferrite was successfully done by sol gel autocombution technique.
- Good nanocrystalline spinel ferrite material was achieved by simple and cost effective synthesis technique.
- The ordered inverse spinel structure of $Li_{0.5}Fe_{2.5}O_4$ is not influenced by Zr^{4+} substitution.
- The cation distribution suggest that the Zr^{4+} ions prefer octahedral [B] site.
- The elastic properties were estimated by Furrier transform infrared spectroscopy.

Abstract

The present report deals with the structural and elastic behavior of Li^+ and Zr^{4+} substituted spinel ferrites. Nanocrystalline spinel ferrite system of chemical formula $Li_{0.5+0.5x}Zr_xFe_{2.5-1.5x}O_4$ (where, x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) was synthesized by using sol-gel auto combustion method. The as-prepared powder was annealed at 800 °C for 5 h for better crystallinity. The annealed samples were characterized by X-ray diffraction technique and Fourier transform infrared spectroscopy for structural and elastic studies respectively. By applying the full pattern fitting of Rietveld method the x, y, z coordinates of atoms, unit cell dimensions and occupancy of ions were estimated. The lattice parameter was found to decrease after substitution due to increase in electron affinity. Site preferences of cations were obtained by matching experimental and calculated intensity. The characteristic bands of crystallographic sub-lattice for the cubic structure were observed by FTIR spectra.

Introduction

Incredible electric and magnetic properties of spinel ferrite are the in charge of their applications in many fields. These properties intimately depend on the structural arrangement of spinel ferrites [[1], [2], [3]]. The spinel ferrites (AB_2O_4) have two interstitial sites namely, tetrahedral (A) and octahedral [B] sites. By site preferences of different ions spinel ferrite is again classified into three types namely, normal, inverse and mixed. In normal spinel, the (A)-site is occupied by divalent metal (M^{2+}) ion whereas the [B]-site is accommodated by Fe^{3+} ions. The inverse spinel is formed by adopting Fe^{3+} ion at (A)-site whereas the [B]-site is accommodated by Fe^{3+} and divalent metal ion (M^{2+}). In mixed spinel, the Fe^{3+} and M^{2+} ion can found at (A) and [B]-sites randomly. In literature, lithium ferrite with chemical formula, $Li_{0.5}Fe_{2.5}O_4$ has been studied extensively by the researchers. Lithium ferrite is a cubic ferrite, belonging to the group of soft ferrite materials with a square hysteresis loop, high Curie temperature and high magnetization [4,5]. It has numerous technological applications in microwave devices, computer memory chip, magnetic recording, radio frequency coil fabrication, transformer cores, antenna rod, ferrofluids, hyperthermia, promising cathode material in a lithium-ion battery, etc. [[6], [7], [8], [9]]. The cubic spinel structure of lithium ferrite can found in two crystalline forms, i.e., ordered and disordered phase. In the 'ordered' phase (space group $P4_132/P4_332$), the Fe^{3+} ions are at octahedral 12d and tetrahedral 8c sites, and Li^+ ions occupy only the octahedral 4b positions in the cubic primitive unit cell. In 'disordered' phase (space group Fd-3m), the Fe^{3+} ions at tetrahedral 8a positions and Li^+ and Fe^{3+} ions randomly distributed over the 16d octahedral sites [10,11]. Several synthesis techniques were available for the preparation of spinel ferrite nanoparticles [12,13]. By considering their merits and demerits the sol-gel autocombustion techniques have much advantages [14].

One of the convenient ways of improving essential properties of spinel ferrites is the substitution of a suitable cation such as Ni^{2+}, Al^{3+}, Ti^{4+}, etc. [[15], [16], [17], [18]]. Substitution of zirconium increases the high-frequency response of ferrites; this has gained considerable importance in recent years because of Gigahertz range applications at present. The addition of zirconium produces dilute spin glass behavior in ferrites and can enhance the frequency range of lithium ferrite. Although many researchers give out with the modification of both lithium and zirconium ions in spinel ferrite, the study of substitution of Zr^{4+} and Li^+ in $(A)[B_2]O_4$ spinel type ferrite and found some exciting results [[19], [20], [21]]. Zr^{4+} ions are most often used because they quickly enter the spinel structure and strongly prefer the [B]-sites. Zirconium is known to lower the anisotropy field, which improves the microstructure of the lithium ferrite. Thus, in the present study, by considering $Li_{0.5}Fe_{2.5}O_4$ as a base compound we have increased the Li^+ and Zr^{4+} ions are introduced systematically.

In view to study the impact of Zr^{4+} ions on structural properties of lithium ferrite, we directed to synthesize Zr^{4+} substituted series by sol-gel auto combustion route and to investigate their structural and morphological properties.

Section snippets

Experimental details

The synthesis of Li^+ and Zr^{4+} substituted MFe_2O_4 spinel ferrite was carried out by sol-gel auto combustion technique. $Li(NO_3)$, $Fe(NO_3)_3$ and $Zr(NO_3)_4$ nitrates of analytical reagent (AR) grade in stoichiometric proportion as a source of Li^+, Fe^{3+} ions and Zr^{4+} ions respectively and citric acid ($C_6H_8O_7$) as a chelating agent procured by Merck (~99.99% purity) were used for the synthesis without further purification. The oxidants were dissolved separately in the minimum amount of distilled water and …

Thermal analysis

The calcination process of lithium ferrite (LZ-1) was analyzed by TGA curve (Fig. 2). The first ~8% weight loss around 180 °C and the second ~20% weight loss before 400 °C corresponds to the solvent evaporation and the release of nitrogen gas respectively. The last ~35% weight loss with a sharp exothermic peak at ~800 °C is associated with the oxidation-decomposition. Meanwhile, the weight decrease continues with the total weight loss of ~70%, indicating the formation of lithium ferrite.…

Conclusion

The synthesized samples show ordered inverse spinel structure with $P4_332$ space group. The lattice parameter decreased after substitution of larger ions in the lithium ferrite. The cation distribution suggested that the tetravalent zirconium ion strongly prefer octahedral site. The ordered spinel structure and CD evident that most of the Li^+ ions are also accommodating [B] site, whereas the Fe^{3+} ions are distributed over both (A) and [B] sub-lattices. The agglomerated spherical morphology with...

Recommended articles

References (43)

A. Raut *et al.*

Synthesis, structural investigation and magnetic properties of Zn^{2+} substituted cobalt ferrite nanoparticles prepared by the sol–gel auto-combustion technique

J. Magn. Magn Mater. (2014)

A.V. Humbe *et al.*

Rietveld refinement, morphology and superparamagnetism of nanocrystalline $Ni_{0.70-x}Cu_xZn_{0.30}Fe_2O_4$ spinel ferrite

Ceram. Int. (2018)

Z.A. Gilani *et al.*

New $LiCo_{0.5}Pr_xFe_{2-x}O_4$ nanoferrites: prepared via low cost technique for high density storage application

Ceram. Int. (2018)

J. Huang *et al.*

Enhancing the electrochemical performance of Li-rich layered oxide $Li_{1.13}Ni_{0.3}Mn_{0.57}O_2$ via WO3 doping and accompanying spontaneous surface phase formation

J. Power Sources (2018)

M.L. Mane *et al.*

Modifications in structural, cation distribution and magnetic properties of 60Co gamma irradiated Li-ferrite

Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms (2011)

S. Dey *et al.*

Preparation and characterization of nanocrystalline disordered lithium ferrite by citrate precursor method

J. Magn. Magn Mater. (2004)

A.V. Humbe *et al.*
Impact of Jahn Teller ion on magnetic and semiconducting behaviour of Ni-Zn spinel ferrite synthesized by nitrate-citrate route
J. Alloy. Comp. (2017)

S. Deshmukh *et al.*
Urea assisted synthesis of Ni1− xZnxFe2O4 (0≤ x≤ 0.8): magnetic and Mössbauer investigations
J. Alloy. Comp. (2017)

M.A. Dar *et al.*
Synthesis and characterization of nano-sized pure and Al-doped lithium ferrite having high value of dielectric constant
J. Alloy. Comp. (2010)

M. Javed Iqbal *et al.*
Structural, electrical and magnetic properties of Zr–Mg cobalt ferrite
J. Magn. Magn Mater. (2008)

View more references

Cited by (21)

Impact of Zn doping on the dielectric and magnetic properties of CoFe<inf>2</inf>O<inf>4</inf> nanoparticles
2022, Ceramics International

Show abstract

Influential trivalent ion (Cr³⁺) substitution in mixed Ni–Zn nanoferrites: Cation distribution, magnetic, Mossbauer, electric, and dielectric studies
2022, Ceramics International

> *Citation Excerpt :*
>
> …Three different (h k l) planes, i.e., (2 2 0), (4 0 0) and (4 2 2) were taken into consideration for the calculation of intensity ratios. Some cation distribution sensitive peak intensity ratios [27,28], such as I400/I220, I422/I220, and I422/I400, were used for estimation of the cation distribution. The different intensity ratio combinations (I400/I220), (I422/I220), and (I422/I400) were considered for the cations at tetrahedral and octahedral sites, and a comparison was made with the observed intensity ratio.…

Show abstract

Visible light photocatalytic activity of magnetically diluted Ni–Zn spinel ferrite for active degradation of rhodamine B

2021, Ceramics International

Show abstract

Impact of trivalent metal ion substitution on structural, optical, magnetic and dielectric properties of Li<inf>0.5</inf>Fe<inf>2.5</inf>O<inf>4</inf> thin films

2019, Physica B: Condensed Matter

> *Citation Excerpt :*
>
> ...The replacement of Fe3+ ions with Al3+ ions at octahedral sites having different ionic radius and atomic mass, is the important reason of the observed shift in the band position [33]. Our previous study of Zr doped lithium ferrite nanoparticles shows that, the Li and Fe ions both occupy tetrahedral and octahedral site [34]. Also, Al can occupy octahedral [B] sites [35]....

Show abstract

Critical behavior in Ni <inf>0.15</inf> Cu <inf>0.15</inf> Zn <inf>0.7</inf> Fe <inf>2</inf> O <inf>4</inf> spinel ferrite

2019, Ceramics International

> *Citation Excerpt :*
>
> ...Spinel ferrites possess the general stoichiometry AB2O4, where A represents a divalent cation, such as Ni, Cu, Zn, Co, Mg, Mn, etc., and B stands for the trivalent cation Fe [4]. As per the cation distribution (CD, which can be obtained by X-ray diffraction, Mössbauer and magnetization methods) [5] at the tetrahedral and octahedral positions, spinel ferrites are classified into three types [5], i.e., normal, inverse and mixed. Several studies have revealed that the CD in the tetrahedral and octahedral sub-lattices of AB2O4-type ferrites has a decisive impact on various properties, such as the microstructure, magnetism, permeability and electronic resistivity [6–9]....

Show abstract

Effects of Ce³⁺ doping on the structural, magnetic and hyperfine properties of cobalt ferrite nanoparticles ↗

2024, Indian Journal of Physics

View all citing articles on Scopus ↗

View full text